Effect of multiple GAC reactivations on disinfection byproduct precursor removal


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Abstract: The objective of this study was to compare the adsorption capabilities of the virgin carbon to the twelve and five times reactivated granular activated carbon (GAC). From a water treatment plant operator’s perspective, there were very few practical differences in adsorption among the carbons tested for total organic carbon (TOC) and disinfection byproduct (DBP) precursors. However, some overall trends were observed. The GAC that was regenerated 5 times (R5) generally showed greater DBP precursor adsorption than the other GACs especially at the beginning of the runs. In some cases the carbon that was reactivated 12/13 times (R12 and R13) adsorbed slightly less DBP precursors than the other GACs especially in the latter part of the runs. The virgin (V) carbon performed better than the other GACs relative to DBP precursor removal in the latter part of the runs.

Keywords: Disinfection byproduct precursor removal; granular activated carbon; reactivation

Introduction

In October, 1992, the Greater Cincinnati Water Works (GCWW) initiated a new unit treatment process at the Richard Miller Treatment Plant (RMTP) – GAC adsorption. GCWW’s GAC facility is one of the world’s largest GAC facilities for drinking water treatment. This facility has twelve post-filter GAC adsorbers and two multiple hearth furnaces for on-site reactivation. Each GAC contactor contains approximately 595 m³ (21,000 ft³) of GAC and each furnace is capable of reactivating approximately 18,150 km (40,000 lbs) of exhausted GAC/day. The GAC process was installed to protect against spills on the industrial Ohio River source and to reduce DBP precursors.

Between October 1992 and November 1998, the original GAC completed twelve cycles of adsorption and subsequent reactivation. Additionally, GAC purchased in 1995 was reactivated separately and had completed five cycles of adsorption and subsequent reactivation by 1998. Contactors containing virgin GAC were being placed in service routinely to replace carbon lost during reactivation. After seven years of GAC adsorption and reactivation, GCWW had three different types of GAC: (1) a lower density GAC with twelve reactivation cycles, (2) a somewhat higher density GAC that had undergone five reactivation cycles and (3) a high density virgin GAC. Considerable differences in iodine number, effective size and abrasion number were noted among these carbon types. Pore volume characteristics indicated that the reactivated GACs contained more mesopore volume and less micropore volume than the virgin GAC, Figure 1 (Moore et al., 2001). These physical changes in the GAC raised questions concerning the selectivity of adsorption and adsorption capacity of the reactivated GAC.

After the first few years of service, GCWW had kept each of the carbons separated by replacing carbon losses with make up carbon from GAC contactors with similar physical characteristics. This separation created a unique opportunity to test the effects of reactivation on GAC structure and adsorption capability. GCWW sought to find a cost effective solution that optimized the GAC process and balanced the removal of DBP precursors and SOCs.
In 1999 GCWW and the Pennsylvania State University (Penn State) were awarded an American Water Works Research Foundation (AwwaRF) grant. The general objective of the grant was to compare the physical characteristics and adsorption capabilities of the virgin carbon to the twelve and five times reactivated GACs and develop reactivation strategies (Moore et al., 2003).

**Materials and methods**

The RMTP is a conventional treatment plant consisting of multiple unit treatment processes in series. Figure 2 depicts the treatment process of the GCWW RMTP during the study period. The RMTP drew water from the Ohio River, pumping averaging 454 m$^3$/d (120 MGD) during the study. Raw water turbidity averaged 24 NTU and TOC – 2.7 mg L$^{-1}$ during the study, both varying seasonally.

An average of 12.7 mg L$^{-1}$ alum was added to the water before sedimentation during the study. During this time a cationic polymer also was added at a dose averaging 1.7 mg L$^{-1}$ to improve sedimentation and filtration. The water was then flocculated in three-stage
tapered flocculation basins and settled in lamella plate-pack settlers. During the study period the lamella facility removed most of the solids and some of the TOC resulting in an average turbidity of 5 NTU and an average TOC of 2.4 mg L\(^{-1}\). The water then passed through two settling and storage reservoirs, 142,320 m\(^3\) (376-MG) total. Water exiting these structures had an average turbidity of 2 NTU and an average TOC of 2.3 mg L\(^{-1}\) during the study. The water leaving the reservoirs passed into two parallel secondary clarification basins, 98,400 m\(^3\) (26-MG). Water exiting these structures was similar in water quality to the settled water.

This water, then, served as influent to 47 rapid sand filters. The filters are constant rate and were operated at 102 L/m\(^2\).min (2.5 gpm/ft\(^2\)). The filtered water had an average turbidity of 0.12 NTU. No disinfecting agents were added prior to filtration and the filters were biologically active. TOC was reduced slightly through the filters. The TOC of the filter effluent averaged 1.8 mg L\(^{-1}\) during the study.

Filter effluent was sent to the granular activated carbon (GAC) facility. This facility was designed with twelve GAC contactors. With eleven contactors on-line, the facility has a design capacity of 660 m\(^3\)/d (175-MGD) with 15 minutes of empty bed contact time (EBCT), but the facility can treat at rates greater than 830 m\(^3\)/d (220-MGD) with no hydraulic bottlenecks at reasonable EBCTs. The contactors were filled with 3.5 m (11.5 feet) of GAC and operated in a down-flow mode. The empty-bed contact time of the GAC contactors typically averaged about 20 minutes. The contactors used in this study contained approximately 272,150 kg (600,000 lbs) of Filtrasorb 400 purchased from Calgon Carbon Corporation.

After GAC adsorption, the water was disinfected by adding chlorine (Avg. 1.6 mg L\(^{-1}\)) and the pH was further adjusted by the addition of sodium hydroxide (Avg. 8.0 mg L\(^{-1}\)). The TOC of the finished water averaged 0.9 mg L\(^{-1}\) during the study.

Three test contactors were in service from November 16, 1998 to July 1, 1999 (Phase 1). They contained virgin carbon, carbon that had been reactivated five times and carbon that had been reactivated twelve times. The oldest GAC and the virgin GAC were then reactivated and returned to service for the second phase of study. The second phase of service began July 24, 1999 and was completed on November 5, 1999 (Phase 2). This phase, then, included two types of carbon: carbon that had been reactivated one time and carbon that had been reactivated thirteen times. The two distinct start-up seasons were chosen to represent different loading and adsorption conditions. Key water quality parameters differed for the two seasons. Most notably, the two phases had very different influent TOC concentrations. The influent TOC during the first phase varied from 1.2 mg L\(^{-1}\) to 2.3 mg L\(^{-1}\), averaging 1.6 mg L\(^{-1}\). The TOC during the second phase varied from 1.8 mg L\(^{-1}\) to 2.7 mg L\(^{-1}\), averaging 2.2 mg L\(^{-1}\). The carbon contactor influent pHs were similar for the two phases. During the first phase, pH varied from 7.6 to 8.5, averaging 8.1; during the second phase, pH varied from 7.6 to 8.4, averaging 8.0. Temperature also varied, as expected, during the two phases. During Phase 1, temperature varied from 4 to 27°C, averaging 13°C. Temperature from Phase 2 varied from 16 to 31°C, averaging 24°C. These differences in water quality parameters created the desired differences in precursor loading and adsorption.

DBP precursors were monitored by using a simulated distribution system and maximum formation potential testing. The simulated distribution approach involved holding the samples for three days (maximum system detention) under operating conditions. Coolers with a flow-through water system kept the samples at distribution system temperature. Chlorine was dosed at plant levels (average of 1.6) and pH was set at 8.5 (plant target). Maximum formation potential conditions were set at reasonable extremes. The samples were held for seven days at a temperature of 30°C. Chlorine was dosed at 15 mg L\(^{-1}\) and pH was held at 9.5. In both cases the chlorine was quenched with sodium thiosulfate (DeMarco et al.,
The samples were analyzed by gas chromatographic techniques using purge and trap concentration. Total trihalomethanes (TTHMs) were monitored at both conditions. Haloacetic acids (HAA5s) were monitored by the simulated distribution (SD) approach. TOC was also monitored throughout the project.

As was mentioned previously, the influent TOC between the two phases differed significantly. Breakthrough curves also differed accordingly. The TOC during the first phase varied from 1.2 mg L\(^{-1}\) to 2.3 mg L\(^{-1}\) averaging 1.6 mg L\(^{-1}\). The TOC during the second phase varied from 1.8 mg L\(^{-1}\) to 2.7 mg L\(^{-1}\), averaging, 2.2 mg L\(^{-1}\). The pH, ranges and averages were similar for the two phases, but temperature varied, as expected.

**Results and discussion**

A slightly modified version of the comparison table used in AWWARF Report 90615 (Summers *et al.*, 1992) was used to compare the relative adsorption of the GACs for each parameter, Table 1. Additionally, the number of days required for effluent concentrations to reach organic levels of regulatory significance or a GCWW treatment goal were also considered in the evaluation, Table 1. In the case of HAA5s the chlorinated effluent concentrations did not reach levels of regulatory concern, so 15 µg L\(^{-1}\) (1/4 of the proposed MCL) was chosen. GCWW’s TOC treatment goal of 1.0 mg L\(^{-1}\) was chosen as a point of reference for comparing the GACs relative to TOC adsorption. Extrapolations and the means of multiple points were used when the data did not exhibit a smooth curve near the critical level.

In Phase 1, R5 performed slightly better relative to TOC adsorption than the other carbons at the beginning of the run, Figure 3. R5 performed similarly to V in the middle of the run and less well than V at the end of the run, Figure 3, Table 1. R12 performed similarly to V at the beginning of the run, but performed slightly worse than the other GACs through the rest of the run, Figure 3, Table 1. The virgin effluent reached 1.0 mg L\(^{-1}\) TOC in 91 days, R5 in 89 days and R12 in 81 days.

In Phase 2, R1 performed slightly better relative to TOC adsorption than R12 throughout the run, Figure 4, Table 1. R1 effluent reached 1.0 mg L\(^{-1}\) in 32 days, R13 in 23 days.

TOC removal ranged from 20 to 85% exhibiting the same general trends as noted in the breakthrough curves.

In Phase 1, R5 performed the best in adsorption of maximum total trihalomethane formation potential (MTTHMFP) at the beginning and middle of the run. V was the best at the end of the run. R12 was similar to V at the beginning of the run, but was the worst at the middle and end of the run. R5 reached 80 µg/L MTTHMFP in 82 days, V in 63 days and R12 in 57 days, Figure 5, Table 1. R5 reached 40 µg L\(^{-1}\) MTTHMFP in 26 days, V and R12 reached 40 µg L\(^{-1}\) MTTHMFP in 23 days, Table 1.

In Phase 2, R1 and R13 performed similarly in MTTHMFP adsorption throughout the run with R13 being slightly better in the middle and R1 being slightly better in the end, Figure 6, Table 1. R13 reached 80 µg L\(^{-1}\) MTTHMFP in 71 days, R1 in 64 days. R13 reached 40 µg L\(^{-1}\) MTTHMFP in 23 days, R1 in 16 days, Table 1.

MTTHMFP removal ranged from 30 to 90% with the same trend as noted in the MTTHMFP breakthrough curves.

In Phase 1, R5 performed the best in SDTTHM precursor removal in the beginning and middle of the run, but was not as good as V at the end of the run. R12 was equal to V in SDTTHM precursor removal at the beginning and middle of the run, but was the worst at the end of the run, Figure 7, Table 1. V reached 40 µg L\(^{-1}\) SDTTHM in the chlorinated effluent in 161 days, R5 in 160 days and R12 in 151 days, Table 1.

In Phase 2, R1 was slightly better in SDTTHM precursor removal throughout, Figure 8, Table 1. R1 reached 40 µg L\(^{-1}\) SDTTHM in the chlorinated effluent in 70 days, R13 in 60 days, Table 1.
**Table 1** Breakthrough curve comparison

<table>
<thead>
<tr>
<th>Phase</th>
<th>Beginning</th>
<th>Middle</th>
<th>End</th>
<th>Days to reach 1 mg/L (TOC)</th>
<th>Days to reach 80 µg/L (TTHM)</th>
<th>Days to reach 40 µg/L (TTHM)</th>
<th>Days to reach 15 µg/L (HAA5)</th>
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<tr>
<td><strong>Phase 1</strong></td>
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<td></td>
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<tr>
<td>TOC</td>
<td>R5=V=R12</td>
<td>R5=V&lt;R12</td>
<td>V&lt;R5&lt;R12</td>
<td>V=91; R5=89; R12=81</td>
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<tr>
<td>MTTHMFP</td>
<td>R5&lt;R12&lt;V</td>
<td>R5&lt;V&lt;R12</td>
<td>V&lt;R5&lt;R12</td>
<td>R5=82; V=63; R12=57</td>
<td>R5=26; V=23; R12=23</td>
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<tr>
<td>SDTHHM</td>
<td>R5&lt;V=R12</td>
<td>R5&lt;V=R12</td>
<td>V&lt;R5&lt;R12</td>
<td>V=161; R5=160; R12=151</td>
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<tr>
<td>SDHAA5</td>
<td>R5&lt;V=R12</td>
<td>R5&lt;V&lt;R12</td>
<td>V&lt;R5&lt;R12</td>
<td></td>
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<td></td>
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<tr>
<td>TOC</td>
<td>R1&lt;R13</td>
<td>R1&lt;R13</td>
<td>R1&lt;R132</td>
<td>R1=32; R13=23</td>
<td></td>
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<tr>
<td>MTTHMFP</td>
<td>R1=R13</td>
<td>R13&lt;R1</td>
<td>R1&lt;R13</td>
<td>R13=71; R1=64</td>
<td>R13=23; R1=16</td>
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<tr>
<td>SDTHHM</td>
<td>R1&lt;R13</td>
<td>R1&lt;R13</td>
<td>R1&lt;R13</td>
<td>R1=70; R13=60</td>
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<tr>
<td>SDHAA5</td>
<td>R1&lt;R13</td>
<td>R1&lt;R13</td>
<td>R13&lt;R1</td>
<td></td>
<td>R13=68; R1=67</td>
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</table>
In Phase 1, R5 performed the best in SDHAA5 precursor removal in the beginning and middle of the run, but not as well as V at the end of the run, Figure 9, Table 1. R12 was the worst in SDHAA5 precursor removal throughout. In neither run did the chlorinated effluent HAA5 levels reach the 60 or 30 µg L\(^{-1}\) SDHAA5 USEPA target regulatory levels, so 15 µg L\(^{-1}\) was chosen as a point of reference. R5 reached 15 µg L\(^{-1}\) SDHAA5 in the chlorinated effluent at 160 days, V at 158 days and R12 at 150 days, Table 1.

In Phase 2, R1 did a better job at removing SDHAA5 precursors at the beginning and middle of the run than R13, at the end of the run, however, an unusually high R1 effluent value caused R13 to be ranked higher, Figure 10, Table 1. R13 reached 15 µg L\(^{-1}\) of SDHAA5 precursor in 68 days, R1 in 67 days.
The differences were slight among the carbons, but trends showed that R5 adsorbed the precursors best at the beginning of the run, V performed the best at the end of the runs and R 12/13 performed slightly worst overall. All carbons were acceptable for TOC and DBP precursor removal at GCWW.

Conclusions
From a water treatment plant supervisor’s perspective, there were very few practical differences in adsorption among the carbons tested for TOC and DBP precursors. However, some overall trends were observed. These trends give some valuable insight into the
differences in adsorption mechanism among the GACs when considered with the porosity and charge data as presented by the data collected at Penn State (Moore et al., 2003). The three major trends were:

1. The GAC that was regenerated 5 times (R5) generally showed greater DBP precursor adsorption than the other GACs especially at the beginning of the runs.

2. In some cases the carbon that was reactivated 12/13 times (R12 and R13) adsorbed slightly less DBP precursors than the other GACs especially in the latter part of the runs.

3. The virgin (V) carbon performed better than the other GACs relative to DBP precursor removal in the latter part of the runs.

This work should give water treatment operators confidence that the reactivation process is not greatly affecting the adsorption of DBP precursors.

References

